contents of the trap warmed to room temperature and remotely agitated from behind a suitable barricade. In this manner high local concentrations of water, which could lead to the production of significant quantities of XeO_3 and violent explosions, were avoided. The solutions were used immediately after their preparation to form the $XeOF_3^+$ and XeO_2F^+ salts as described below.

Preparation of $XeF_3^+Sb_2F_{11}^-$ and $XeF_3^+SbF_6^-$. A quantity of SbF_5 (3.773 g, 17.41 mmol) was added to 0.883 g (4.26 mmol) of XeF_4 in a glass ampoule. A Teflon valve was attached and the ampoule and contents was warmed to 50° to effect dissolution. The resulting yellow-green solution crystallized immediately upon cooling to room temperature. Excess SbF_5 was removed under vacuum at room temperature and pumping continued until constant weight was obtained (~36 hr). The final weight of product was 2.755 g and corresponded to $XeF_4 \cdot 2.03SbF_5$. The combining ratio as well as the elemental analyses is consistent with the formulation of this compound as $XeF_3^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 41.51; Sb, 38.00; Xe, 20.49. Found: F, 41.22; Sb, 38.37; Xe, 20.75.

A quantity of $XeF_3^+Sb_2F_{11}^-$ (0.251 g, 0.391 mmol) was fused with XeF_4 (0.286 g, 1.381 mmol) for 1 hr at 80°. Excess XeF_4 was removed under vacuum at room temperature. The elemental analyses are consistent with the formulation $XeF_3^+SbF_6^-$. *Anal.* Calcd: F, 40.33; Sb, 28.71; Xe, 30.96. Found: F, 40.55; Sb, 28.32; Xe, 30.60.

Attempts were made to prepare $Xe_2F_7^+SbF_6^-$ by a method analogous to that used previously to prepare $Xe_2F_3^+SbF_6^-$.[16] In a typical experiment, 0.264 g (1.217 mmol) of SbF_5 in 5.565 g of HF was added to 0.504 g (2.324 mmol) of XeF_4 in a Teflon tube through a Kel-F Y piece. The XeF_4 dissolved at room temperature to give a bright yellow solution. The HF solvent was slowly pumped off at room temperature to give a pale yellow-green crystalline solid. A portion of the sample was transferred to a glass tube and examined by Raman spectroscopy and was shown to contain a significant amount of unreacted XeF_4. Excess XeF_4 was pumped off under vacuum at room temperature and a suitable crystal was selected from the remaining material and subjected to a single-crystal X-ray structure determination. The Raman spectrum of the crystal used in the structure analysis was identical with the spectrum of the bulk material. The results of the X-ray crystal structure determination, which has been published elsewhere,[11] show that this material was $XeF_3^+SbF_6^-$. No evidence for the formation of $Xe_2F_7^+SbF_6^-$ was obtained in the present work.

Preparation of $XeOF_3^+Sb_2F_{11}^-$ and $XeOF_3^+SbF_6^-$. A solution containing 1.307 g (5.853 mmol) of $XeOF_4$ in 1.991 g of HF was poured through a Kel-F Y piece into a preweighed Teflon trap and valve assembly containing 3.516 g (16.22 mmol) of SbF_5. The HF solvent was pumped off at room temperature and pumping continued for 8 hr. The weight of the white solid remaining in the trap was 3.800 g and corresponded to the composition $XeOF_4 \cdot 1.965SbF_5$. The elemental analyses as well as the combining ratio support the formulation of this compound as $XeOF_3^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 40.50; Sb, 37.07; Xe, 19.99. Found: F, 40.74; Sb, 37.34; Xe, 19.72.

The 1:1 compound $XeOF_3^+SbF_6^-$ was synthesized by allowing 0.529 g (2.439 mmol) of SbF_5 to react with 1.053 g (4.717 mmol) of liquid $XeOF_4$ at room temperature in a preweighed Teflon tube equipped with a Teflon valve. Excess $XeOF_4$ was recovered by pumping the liquid into a Kel-F cold trap assembly cooled to −196°. The resulting white solid was pumped on for 1 additional hr at room temperature. The elemental analyses are in accord with the formulation $XeOF_3^+SbF_6^-$. *Anal.* Calcd: F, 38.86; Sb, 29.84; Xe, 27.67. Found: F, 38.65; Sb, 28.03; Xe, 29.60.

Preparation of $XeO_2F^+Sb_2F_{11}^-$. The techniques used for the formation of the $XeO_2F^+Sb_2F_{11}^-$ were directly analogous to those employed in the synthesis of $XeOF_3^+Sb_2F_{11}^-$. In one experiment 1.392 g (6.914 mmol) of XeO_2F_2 dissolved in 1.550 g of HF was added to 6.452 g (29.77 mmol) of SbF_5. Pumping off the bulk of the solvent at room temperature yielded an SbF_5 solution of what was later shown to be XeO_2F^+. This solution was unstable at room temperature and slowly evolved oxygen gas. Pumping this solution to dryness yielded a light yellow product severly contaminated with $XeF^+Sb_2F_{11}^-$.[33] In another experiment, stoichiometric amounts of XeO_2F_2 (0.918 g, 4.563 mmol, dissolved in 1.185 g of HF) and SbF_5 (1.974 g, 9.11 mmol) were combined, mixed, and immediately pumped to dryness at room temperature. The product was a white solid and had a weight (2.891 g) corresponding to $XeO_2F_2 \cdot 2.00SbF_5$. The elemental analyses are also in agreement with the formulation $XeO_2F^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 35.91; Sb, 38.35; Xe, 20.69. Found: F, 35.64; Sb, 38.67; Xe, 20.43. No Raman band attributable to XeF^+ was observed in material prepared by the latter method.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work.

Registry No. SbF_5, 7783-70-2; XeF_4, 13709-61-0; $XeF_3^+Sb_2F_{11}^-$, 39797-62-1; $XeF_3^+SbF_6^-$, 39797-63-2; $XeOF_4$, 13774-85-1; $XeOF_3^+Sb_2F_{11}^-$, 39797-64-3; $XeOF_3^+SbF_6^-$, 39797-65-4; XeO_2F_2, 13875-06-4; $XeO_2F^+Sb_2F_{11}^-$, 52078-91-8.

(33) An intense Raman band at 619 cm^{-1} due to the Xe–F stretching mode of XeF^+ in $XeF^+Sb_2F_{11}^-$ was observed.

Contribution from Rocketdyne, A Division of Rockwell International,
Canoga Park, California 91304

Infrared and Raman Spectra of Trifluoromethyl Perchlorate

CARL J. SCHACK* and KARL O. CHRISTE

Received March 5, 1974 AIC401486

The gas-phase infrared spectrum and the liquid-phase Raman spectrum of trifluoromethyl perchlorate have been recorded. The spectra show that CF_3OClO_3 contains a covalent monodentate perchlorato group. A total of 19 fundamental vibrations out of 21, expected for a model of symmetry C_s with hindered rotation, were observed and assigned.

Introduction

Few covalent perchlorates are known. Among these are free perchloric acid, $HOClO_3$, and its anhydride, $O_3ClOClO_3$, both of which have been known for many years.[1] More recently the halogen perchlorates $FOClO_3$,[2] $ClOClO_3$,[3] $BrOClO_3$,[4] $Cs^+Br(OClO_3)_2^-$,[5] $I(OClO_3)_3$,[6] and $Cs^+I(OClO_3)_4^-$ [6] have been reported. Alkyl perchlorates are also known but are very treacherous materials[1] and therefore have not been investigated extensively. While spectroscopic studies of O_3-

(1) J. C. Schumacher, "Perchlorates", ACS Monograph Series, No. 146, Reinhold, New York, N. Y., 1960.

(2) G. H. Rohrback and G. H. Cady, *J. Amer. Chem. Soc.*, 69, 677 (1947).

(3) C. J. Schack and D. Pilipovich, *Inorg. Chem.*, 9, 1387 (1970).

(4) C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, *Inorg. Chem.*, 10, 1078 (1971).

(5) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 13, 1452 (1974).

(6) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 11, 1682 (1972).

$ClOClO_3$,[7,8] $HOClO_3$,[9] and the halogen perchlorates[5,6,10] have been completed, alkyl perchlorates remain unexamined. Renewed interest in the synthesis of new covalent perchlorates[11,12] has shown that perhalogenated alkyl derivatives can be prepared, are stable, and are thus amenable to further study.

For spectroscopic work on alkyl compounds it is best to study the simplest example in order to avoid interference from bands due to large alkyl groups. Recently we succeeded in synthesizing[13] the novel fluorocarbon perchlorate trifluoromethyl perchlorate. Owing to its simplicity this compound is ideally suited for a systematic study of its vibrational spectrum.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Trifluoromethyl perchlorate was prepared from CF_3I and $ClOClO_3$ as reported[13] and was purified by several fractional condensations. The purity of the sample used for this study was verified by its mass spectrum and tensiometric homogeneity. Infrared absorbing impurities were not detected. Pure CF_3OClO_3 is stable and can be manipulated with much less difficulty than any of the halogen perchlorates. A gas sample stored in a stainless steel vessel at room temperature for nearly 2 years was not noticeably changed.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5- or 10-cm path length fitted with AgCl or AgBr windows. The instrument was calibrated by comparison with standard calibration points.[14] The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å line of an Ar ion laser as the exciting line and a Claassen filter[15] for the elimination of plasma lines. Sealed quartz tubes (~ 2-mm i.d.) were used as sample containers for the liquid in the transverse-viewing–transverse-excitation technique. The Raman spectra were recorded at −100° using a device similar to that previously described.[16]

Results and Discussion

Caution! Perchlorates are generally shock sensitive and must be treated with due care. Although trifluoromethyl perchlorate appears quite stable, deflagrations were occasionally encountered in the course of its synthesis.

Vibrational Spectrum. Figure 1 shows the infrared spectrum of gaseous trifluoromethyl perchlorate at several pressures and the Raman spectrum of the liquid. Table I lists the observed frequencies together with their assignments.

Structural Model. In principle several isomeric structures are possible for a compound with the empirical composition CF_3ClO_4. All the observed properties, *i.e.*, low melting point, bp 9.5°, Trouton constant 23.3, vapor-phase mol wt 167, and nmr-equivalent fluorines, together with the direct synthetic method, are consistent with a structure containing a CF_3 group linked to a ClO_4 group through one of the oxygens. Such a structure would be expected to have a bent C–O–Cl link much like the previously studied[2-10] covalent perchlorates and to resemble spectroscopically a mixed ether, $B_3A\text{-}O\text{-}CD_3$. Therefore, CF_3OClO_3 should possess structure I of symmetry C_s assuming one F and one double-bonded oxygen atom to be located in the COCl plane. Assuming free rotation of the CF_3 and ClO_3 groups, the molecule would also possess C_s symmetry but some of the XY_3 modes would be degenerate. Assuming hindered rotation a nine-atom molecule of C_s symmetry should exhibit 21 fundamental modes of vibration, all active in both the infrared and the Raman spectra. Of these, 13 belong to species A′ and can be either polarized or depolarized, while 8 belong to species A″ and should be depolarized. The 21 fundamental vibrations arise from 3 skeletal motions and 9 modes each for the CF_3 and the ClO_3 groups. The 9 motions each of the CF_3 and ClO_3 groups may be described as 3 stretching modes, 3 deformational modes, 2 rocking fundamentals, and 1 torsional oscillation. Torsional modes for CF_3[17] and ClO_3[7] groups generally occur at quite low frequencies (beyond the range of our infrared measurements), are weak, and usually are not observed. No evidence for the two torsional fundamentals was found and they will not be considered further in our discussion.

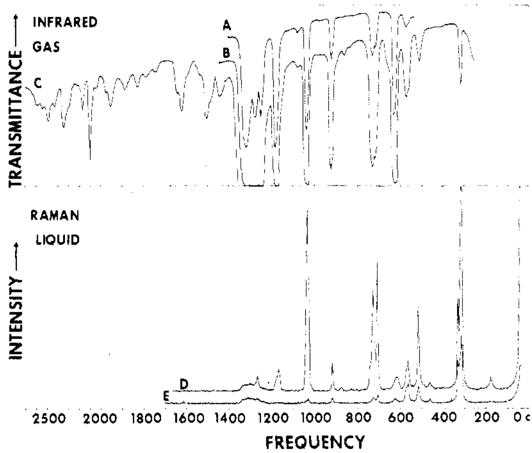
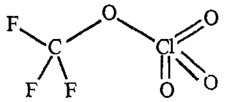


Figure 1. Vibrational spectra of CF_3OClO_3. Infrared spectrum of the gas: A, 5 mm in a 5-cm path length cell with AgCl windows; B and C, 18 and 125 mm, respectively, in a 10-cm path length cell with AgBr windows. Raman spectrum of the liquid at ~−100°: D, incident polarization perpendicular; E, incident polarization parallel; the spectral slit width used was 3 cm^{-1}.



I

Assignment of Stretching Modes. Investigations[17,18] of trifluoromethyl compounds have shown that the CF_3 stretching fundamentals lie in the frequency range 1400–1100 cm^{-1}. Similarly for ClO_3 stretching modes, the frequency range 1350–1000 cm^{-1} has been established.[7,10] In spite of this frequency range overlap, assignments can be made to the modes belonging to the CF_3 and the ClO_3 groups, respectively. The two antisymmetric ClO_3 stretches usually are almost degenerate and splitting into the individual modes is

(7) J. D. Witt and R. M. Hammaker, *J. Chem. Phys.*, **58**, 303 (1973).

(8) A. C. Pavia, J. Roziere, and J. Potier, *C. R. Acad. Sci., Ser. C*, **273**, 781 (1971).

(9) P. A. Giguere and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

(10) K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, **10**, 1589 (1971).

(11) K. Baum, *J. Amer. Chem. Soc.*, **92**, 2927 (1970).

(12) C. J. Schack, D. Pilipovich, and J. F. Hon, *Inorg. Chem.*, **12**, 897 (1973).

(13) C. J. Schack, D. Pilipovich, and K. O. Christe, *Inorg. Nucl. Chem. Lett.*, **10**, 449 (1974).

(14) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).

(15) H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.*, **8**, 23 (1969).

(16) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, **24**, 291 (1970).

(17) C. V. Berney, *Spectrochim. Acta*, **21**, 1809 (1965).

(18) J. R. Durig and D. W. Wertz, *J. Mol. Spectrosc.*, **25**, 467 (1968).

Table I. Vibrational Spectra of CF_3OClO_3[a]

Obsd freq, cm^{-1}, and intens[b]		Assignment in point group C_s and approx description of mode
Infrared (gas)	Raman (liquid)	
2595 vw		$\nu_2 + \nu_{14} = 2595$ (A″)
2547 vw		$\nu_1 + \nu_{15} = 2549$ (A″)
2486 w		$2\nu_{15} = 2482$ (A′)
2435 vw		$\nu_2 + \nu_3 = 2436$ (A′)
2345 w		$2\nu_3 = 2342$ (A′)
2290 vw		$\nu_2 + \nu_4 = 2293$ (A′)
2167 vw		$\nu_5 + \nu_{15} = 2155$ (A″) or $\nu_2 + \nu_5 = 2179$ (A′)
2093 w		$\nu_3 + \nu_5 = 2085$ (A′)
2038 vw		$\nu_7 + \nu_{14} = 2036$ (A″)
1964 vw		$\nu_1 + \nu_{16} = 1968$ (A″) or $\nu_2 + \nu_7 = 1971$ (A′)
1942 w		$\nu_8 + \nu_{14} = 1945$ (A″) or $\nu_7 + \nu_{15} = 1947$ (A″) or $\nu_4 + \nu_5 = 1942$ (A′)
1877 vw		$\nu_3 + \nu_7 = 1877$ (A′)
1831 vw		$2\nu_5 = 1828$ (A′) or $\nu_3 + \nu_{16} = 1831$ (A″) or $\nu_2 + \nu_{17} = 1833$ (A″)
1632 vw		$\nu_5 + \nu_6 = 1638$ (A′) or $\nu_3 + \nu_{18} = 1633$ (A″)
1612 w		$\nu_1 + \nu_{12} = 1622$ (A′) or $\nu_5 + \nu_7 = 1620$ (A′) or $\nu_2 + \nu_{11} = 1604$ (A′)
1495 w		$\nu_4 + \nu_{18} = 1490$ (A″)
1438 vw		$\nu_2 + \nu_{13} = 1443$ (A′) or $\nu_6 + \nu_7 = 1430$ (A′)
1308 vs	1330 (0.2) dp[c]	ν_{14}(A″) ν antisym ClO_3
	1300 (0.3) p	ν_1(A′) ν antisym ClO_3
1265 s	1267 (0.5) p	ν_2(A′) ν antisym CF_3
1241 s	1240 (0.1)	ν_{15}(A″) ν antisym CF_3
1171 vs	1169 (0.8) p	ν_3(A′) ν sym CF_3
1074 vw		$\nu_9 + \nu_{10} = 1072$ (A′)
1028 vs	1031 (7.2) p	ν_4(A′) ν sym ClO_3
914 m	917 (1.1) p	ν_5(A′) ν C–O
	880 (0.1) p	$\nu_9 + \nu_{12} = 880$ (A′)
852 vw		$\nu_{10} + \nu_{11} = 851$ (A′)
829 vvw		$\nu_{10} + \nu_{12} = 826$ (A′)
724 m	726 (4.2) p	ν_6(A′) δ sym CF_3
706 sh (PQR)	708 (5.1) p	ν_7(A′) δ antisym CF_2
660 sh	660 (<0.1)	ν_{16}(A″) δ antisym CF_3
615 s	616 (0.5) p	ν_8(A′) ν O–Cl
568 mw	570 (0.7) dp	ν_{17}(A″) δ antisym ClO_3
560 sh	564 (1.1) p	ν_9(A′) δ antisym ClO_2
512 w	516 (3.2) p	ν_{10}(A′) δ sym ClO_3
	490 (<0.1)	$\nu_{12} + \nu_{13} = 494$ (A′)
463 vvw	462 (0.2) dp	ν_{18}(A″) δ rock CF_3
339 sh	342 (3.5) p	ν_{11}(A′) δ wag CF_3
	320 dp?	ν_{19}(A″) δ rock ClO_3
314 mw	316 (10) p	ν_{12}(A′) δ in-plane C–O–Cl
	178 (0.5) p	ν_{13}(A′) δ wag ClO_3

[a] In addition to the listed infrared absorptions very weak bands were observed having the frequencies 2635, 2455, 2220, 2195, 1893, 1780, 1734, 1533, and 1476 cm^{-1} which can readily be assigned to combination bands and overtones. [b] Uncorrected Raman intensities representing relative peak height. [c] Qualitative polarization measurement.

only observed for liquid or matrix-isolated samples.[10] In the infrared spectrum of the gas, they generally appear as a very intense, somewhat broad band near 1300 cm^{-1} and, therefore, are assigned for CF_3OClO_3 to the strong infrared band at 1308 cm^{-1} (see Figure 1). Furthermore, it is expected that their Raman counterparts would be weak. This is the case as shown in Figure 1. For the liquid also partial separation into the almost degenerate components was noted. The higher frequency band, 1330 cm^{-1}, appears depolarized and is therefore assigned to the A″ antisymmetric ClO_3 stretch, while the 1300-cm^{-1} band appears polarized and is assigned to the corresponding A′ mode. The symmetric ClO_3 stretching vibration is normally found in the range 1060-1000 cm^{-1}, well below the CF_3 stretching mode range and is intense in both the infrared and the Raman spectra. Since only one intense band at 1028 cm^{-1} is noted in this region in both spectra, it is assigned to the symmetric ClO_3 stretching vibration. Further support for this assignment is the high degree of polarization[19,20] of the band in the Raman spectrum.

For the three CF_3 stretching vibrations, there remain three bands in the appropriate infrared region (1265, 1241, 1171 cm^{-1}) all of which are strong as expected. Conversely, they are very weak in the Raman spectrum where it is seen that two of the three are highly polarized and one (1240 cm^{-1}) is probably depolarized. The lower frequency polarized band (1169 cm^{-1}) can be readily assigned to the A′ symmetric CF_3 stretching mode which agrees well with previous assignments.[18,20] The other polarized band (1267 cm^{-1}) is then attributable to the antisymmetric CF_3 stretch of species A′ while the corresponding A″ mode is assigned to the 1240-cm^{-1} band. Thus the assignment of all of the six stretching vibrations is straightforward and can be made with confidence.

Immediately below the region for ClO_3 and CF_3 stretching motions is the area in which C–O stretching vibrations are most likely[18-20] to occur, *i.e.,* approximately between 1000 and 900 cm^{-1}. Figure 1 shows that only one intense band occurs in this region. This band at 914 cm^{-1} is moderately intense in both the infrared and the Raman spectra, exhibits the correct infrared band contour for an A′ mode, and is polarized. All of these observations support its assignment as the C–O stretching fundamental. Comparable C–O bands have been reported at 916 cm^{-1} (average value) for CF_3OOOCF_3[20] and at 915 cm^{-1} for CF_3OCl.[21]

Assignment of Deformational Modes. Inspection of the literature[17,18,20] reveals that for simple CF_3-containing molecules the CF_3 deformation vibrations occur in the range of 720-520 cm^{-1}. Similarly, ClO_3 compounds[7,9,10,22] show deformational modes in the range 600-510 cm^{-1}. In addition, the Cl–O single-bond stretch should occur in this frequency region.[7,9,10] Hence, for CF_3OClO_3 we should expect seven fundamentals in the frequency range 720-510 cm^{-1} in excellent agreement with our observations (see Figure 1 and Table I). Of the seven expected, five belong to species A′ and two to species A″. The latter must be depolarized in the Raman spectrum and arise from the antisymmetric CF_3 and ClO_3 deformations. Of these seven observed bands, only one band (570 cm^{-1}) is clearly depolarized while five (726, 708, 616, 564, and 516 cm^{-1}) are polarized and for one (660 cm^{-1}) the polarization ratio is doubtful owing to its very low intensity. Since for all of the reported ClO_3 compounds, the A″ antisymmetric deformation is moderately intense in both the infrared and the Raman spectra, the more intense one (570 cm^{-1}) of the two apparently depolarized bands is assigned to the A″ antisymmetric ClO_3 deformation, and the very weak one at 660 cm^{-1} is assigned to the A″ antisymmetric CF_3 deformation. The low intensity thereby attributed to this CF_3 mode is not unusual since for similar compounds it is sometimes not even observed.[18,23]

In the series of $XOClO_3$ compounds where X = F,[24] Cl,[10] and Br,[10] the internal Cl–O single-bond stretch results in

---

(19) K. O. Christe, *Spectrochim Acta, Part A,* 27, 463 (1971).

(20) J. D. Witt, J. R. Durig, D. DesMarteau, and R. M. Hammaker, *Inorg. Chem.,* 12, 807 (1973).

(21) C. J. Schack and W. Maya, *J. Amer. Chem. Soc.,* 91, 2902 (1969).

(22) H. H. Claassen and E. H. Appelman, *Inorg. Chem.,* 9, 622 (1970).

(23) P. M. Wilt, Thesis, Vanderbilt University, 1967.

a strong infrared band comparable in intensity to the ClO_3 stretching bands. As seen in Figure 1, there is only one such infrared band (615 cm^{-1}) present in the appropriate frequency range and hence should be assigned to the Cl-O stretching mode. The observed frequency for this band (615 cm^{-1}) is only slightly lower than that noted for the related halogen perchlorates (666-646 cm^{-1}).[10,24]

We are left now with four unassigned bands in the 720-520-cm^{-1} region. The two higher frequency (724 and 706 cm^{-1}) infrared bands are also appreciably stronger than the two lower ones (560 and 512 cm^{-1}). Furthermore these higher frequency vibrations occur beyond the 600-510-cm^{-1} range predicted for ClO_3 deformations. Therefore, they are ascribed to the two unassigned CF_3 A′ deformational modes. Since the 724-cm^{-1} band is of higher intensity in the infrared spectrum, it is assigned to the CF_3 umbrella deformation, while the 706-cm^{-1} band is assigned to the CF_3 scissoring deformation. These assignments are analogous to those of other CF_3 moieties[18,20,25] where similar frequency and intensity relationships have been observed.

By analogy with the corresponding CF_3 deformations, the ClO_3 umbrella deformation should be more intense than the ClO_3 scissoring mode in both the infrared and Raman spectra. Therefore, the 512- and the 560-cm^{-1} bands are assigned to the ClO_3 umbrella and scissoring modes, respectively, in good agreement with previous observations.[7,9,10] It should be noted that for all these compounds the frequency of the ClO_3 umbrella deformation is nearly constant (515 ± 6 cm^{-1}) indicating this mode to be highly characteristic.

There are five fundamental vibrations left unaccounted for. Two of these are the CF_3 and the ClO_3 wagging motion belonging to species A′. Another two are the CF_3 and Cl-O_3 rocking motions of species A″. The fifth fundamental is the C-O-Cl in-plane bending motion which will be considered first. This vibration should occur below 500 cm^{-1} and involve a large change in the polarizability of the molecule. It should therefore appear as an intense Raman band. Since the most intense Raman band in the entire CF_3OClO_3 spectrum occurs at 316 cm^{-1} and is polarized, this frequency must represent this mode. Neither the A′ CF_3 wag nor the A′ ClO_3 wag should produce such a strong Raman band. Comparable data on similar motions in related compounds are extremely limited. Examples that might be useful for comparison are the Cl-O-Cl skeletal bend of $O_3Cl-O-ClO_3$ and the O-O-O bend in the trioxide CF_3OOOCF_3. The former has been assigned[7,8] to a Raman peak at 161 cm^{-1} while the trioxide bend[20] has been attributed to a peak at 286 cm^{-1}. Whereas the latter assignment is in excellent agreement with our assignment for CF_3OClO_3, the former might be incorrect. Based on our data for CF_3OClO_3, we prefer to reassign the Cl-O-Cl bend in Cl_2O_7 to the very intense Raman band at 286 cm^{-1} and attribute the 161-cm^{-1} band to the ClO_3 wagging motion (see below).

As has been remarked by Durig and Wertz[18] and Witt and Hammaker,[7] the precise assignment of $-XY_3$ rocking motions is difficult owing to the wide range of frequencies involved and the paucity of data. Our assignments for the modes are based on the following observations: (i) the two polarized Raman lines must represent the wagging (A′) motions, and the two depolarized lines, the rocking (A″) motions; (ii) all the assigned CF_3 deformations have higher frequencies than the corresponding ClO_3 modes. Consequently, the higher frequency A′ and A″ modes are attributed to the CF_3 group and the lower ones to the ClO_3 group (see Table I).

A band of very low intensity was noted in the Raman spectrum at 490 cm^{-1} but was not observed in the infrared spectrum. We do not believe that this is a fundamental, although that possibility cannot be completely ruled out. It could be due to a combination ($\nu_{12} + \nu_{13} = 494$ cm^{-1}) or perhaps an impurity.

Summary

The observed infrared and Raman spectra of CF_3OClO_3 are in excellent agreement with a structure of symmetry C_s containing a covalent monodentate perchlorato group. The close agreement between the infrared frequencies of the gas and the Raman frequencies of the liquid indicate that no appreciable association occurs in the liquid phase. Observation of two separate antisymmetric stretching modes for both the CF_3 and the ClO_3 groups indicates hindered rotation for both groups. Except for the two torsional modes, all predicted fundaments were observed and assigned and indicate the need for reassigning the two lowest frequency vibrations in Cl_2O_7.

Acknowledgment. We are very pleased to acknowledge support for this work by the Office of Naval Research, Power Branch. Also we are grateful to Dr. L. R. Grant for helpful discussions.

Registry No. CF_3OClO_3, 52003-45-9.

---

[24] H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, 40, 157 (1968).

[25] K. O. Christe and D. Naumann, *Spectrochim. Acta, Part A*, 29, 2017 (1973).